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Study of the early stage of phase separation in polymer solutions

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粘弾性相分離現象の発展過程では、少数相が過渡的に連結したネットワーク状の相分離構造を形成するなど、通常の流体系相分離のパターン形成とは異なる特徴が見出される。その本質は、相分離の初期における高分子による過渡的ゲルの形成にあり、このとき高分子には、相分離の熱力学的力に対抗する力学的応力が、自発的に生じると考えられる。この力学的応力を測定するため、高分子溶液系 PS/DEM (polystyrene/diethyl malonate) 系をサンプルとし、時分割光散乱の手法により相分離の初期過程を観測した。VH 散乱 (力学的応力の空間分布に対応) では四葉のクローバー型の散乱パターンが現れ、高分子鎖に力学的応力が加わっていることを直接的に示唆する結果を得た。また、VV 散乱 (ほぼ濃度の空間分布に対応) と VH 散乱のパターンの時間発展を比較し、相分離の初期過程に特徴の異なる二つのプロセスが存在することを示した。

A novel form of phase separation, *viscoelastic* phase separation (VPS)[1] can occur in binary mixtures. VPS is induced by a strong dynamic asymmetry between the two components, such that the relaxation timescales of the components are well separated. Examples include polymer solutions, colloidal dispersions, protein solutions and micelle dispersions. In the case of polymer solutions, the small solvent molecules relax very much faster than the larger polymer 'macromolecules'. The key feature of VPS is that the slower-molecule-rich phase shrinks in early time and transiently forms network-like structures even if it is the minority phase. These characteristics are fundamentally different from ordinary fluid phase separation. The reason for these characteristics is thought to be that the transient gel is formed by the slower component and has a strong impact on the morphology. Therefore we seek to measure the viscoelastic stress emerged by transient gel formation and to understand the effect of the stress on phase separation process.

To measure the stress formed during VPS, we observed phase separation in polymer solution (polystyrene (PS) and diethyl malonate (DEM)) by VH-scattering (crossed nicole) of time resolved static light scattering. Molecular weight M_w of PS is 3.86×10^6 and concentration of the solution was 2.0 wt%PS. The power-spectrum image we detected was a four-leaf clover pattern (Figure 1). This pattern means that the mechanical stress acted on the polymers and we could

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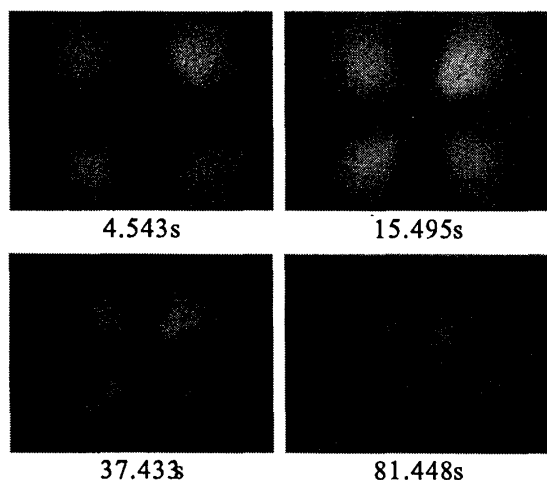


Figure 1: Temporal change of VH-scattering pattern PS/DEM, $M_w\text{PS} = 3.84 \times 10^6$, 2.14 wt%PS, 25.7 °C.

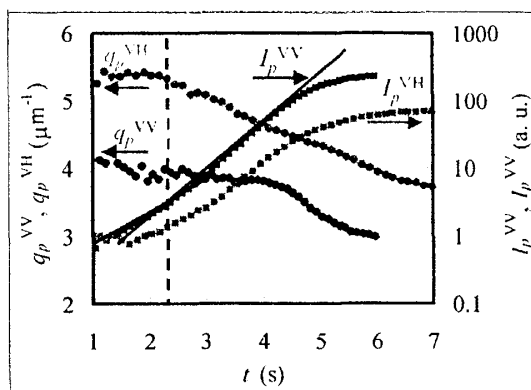


Figure 2: Temporal change of peak wave number q_p and peak intensity I_p of scattering function of VH-scattering, PS/DEM, $M_w\text{PS} = 3.84 \times 10^6$, 2.14 wt%PS, 25.7 °C.

detect birefringence due to the stress on the polymers. Therefore we directly detected the stress that spontaneously arose as a result of stress-diffusion coupling. Furthermore the pattern means that the direction of the stress is random and the spatial distribution of the stress is isotropic. We confirmed that the pattern appeared upon phase separation (at the critical concentration). Figure 2 shows temporal change of the peak wave number q_p and peak intensity I_p of scattering function of VV- and VH-scattering. The early stage of phase separation emerged by about 4 second. It is found that there are two processes in the early stage. The dashed line in the figure refers to a transitional time dividing the two processes. Particularly, after the transitional time, the temporal change of both I_p of VV and of VH accelerates. It seems that diffusion of PS strongly couples with mechanical stress produced spontaneously on the PS upon network formation. We believe that the second processes is related to transient gelation of PS. Furthermore, to clarify the behavior of this new process we carried out the same experiment using another M_w of PS solution. In the presentation, we will explain the details about the experimental results and discuss the relation between the two processes and the transient gelation of PS.

References

- [1] Hajime Tanaka, J. Phys.: Condens. Matter **12** (2000), 207